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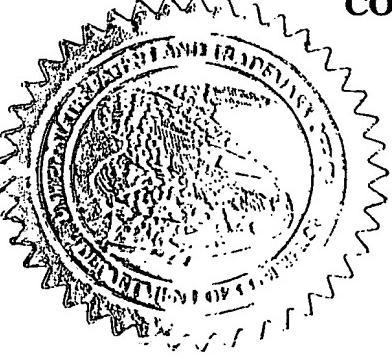
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APPLICATION NUMBER: 60/511,482

FILING DATE: October 15, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/02929

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)		
Given Name (first and middle [if any])		Family Name or Surname
Dong-Kyun Nora		Seo Iancu
		Residence (City and either State or Foreign Country) Phoenix, AZ Scottsdale, AZ
<p><i>Additional inventors are being named on the _____ separately numbered sheets attached hereto</i></p>		
<b>TITLE OF THE INVENTION (500 characters max)</b>		
IMPROVED SYNTHESIS OF METAL-CHALCOGENIDE NANOPARTICLES		
<i>Direct all correspondence to:</i> <b>CORRESPONDENCE ADDRESS</b>		
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<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>		
<input checked="" type="checkbox"/> Specification <i>Number of Pages</i>		<b>4</b>
<input checked="" type="checkbox"/> Drawing(s) <i>Number of Sheets</i>		<b>6</b>
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		<input checked="" type="checkbox"/> CD(s), Number <input type="text"/>
<input checked="" type="checkbox"/> Other (specify)		<input type="text"/> <b>Return Postcard</b>
<b>METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT</b>		
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. <input type="checkbox"/> A check or money order is enclosed to cover the filing fees <input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.		<b>FILING FEE AMOUNT (\$)</b> <b>\$80.00</b>
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. <input type="checkbox"/> No. <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____		

*Respectfully submitted,*

**SIGNATURE**

**SIGNATURE**

Respectfully submitted, [Redacted] 17-15612

Date 10/15/03

**TYPED or PRINTED NAME** Barbara J. Luther

**REGISTRATION NO.**  
*(if appropriate)*  
Rocket Number

**602-230-5502**

33,954

130588.00058 PRC

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By:   
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**CERTIFICATE OF MAILING PURSUANT TO 37 C.F.R. 1.10**

Applicant: Dong-Kyun Seo et al.  
Serial No.: to be determined  
Filed: 10-15-2003  
Title: IMPROVED SYNTHESIS OF METAL-CHALCOGENIDE  
NANOPARTICLES  
Art Unit: to be determined  
Examiner: to be determined  
Docket: 130588.00058 PRO

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Type of Filing:

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- 3) Patent application, four pages
- 4) Laboratory notebook note pages, seven pages
- 5) Drawings, six sheets
- 6) Return receipt postcard

**IMPROVED SYNTHESIS OF METAL-CHALCOGENIDE NANOPARTICLES****BRIEF DESCRIPTION OF THE FIGURES**

[0001] FIG. 1 displays the X-ray powder patterns of CdSe nanoparticles prepared at 200°C. The abbreviation s-CdSe stands for the wurzite form; zb-CdSe is the zinc blend form.

[0002] FIG. 2 shows the UV-Vis absorption and emission spectra of CdSe nanoparticles prepared at 60°C for five hours.

[0003] FIG. 3 shows the emission spectra of CdSe nanoparticles prepared at 60° C for three days.

[0004] FIG. 4 shows the poor emission characteristics of CdSe nanoparticles prepared at 200°C for three days.

[0005] FIG. 5 displays two color photos of beakers with the CdSe samples and a third figure with photoluminescence (emission).

[0006] FIG. 6 displays TEM images of CdSe nanoparticles prepared at 200°C.

**DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT**

[0007] The new preparative method uses boron selenides and sulfides as the source of selenium and sulfur in preparation of metal-chalcogenide nanoparticles in solution. The typical materials that can be prepared include but are not limited to CdSe, CdS, PbSe, PbS, ZnSe, ZnS, to name a few. The method is particularly advantageous for selenides, because the earlier methods (Joo, J. et al, J Amer Chem Soc 2003, 125:11100, "Generalized and Facile Synthesis of Semiconducting Metal Sulfide Nanocrystals;" Peng, X. et al, Patent Publication WO 2003050329, "High Quality Colloidal Nanocrystals and Methods of Preparation of the Same in Non-Coordinating Solvents;" Li, J. et al, J Amer Chem Soc 2003, in press, "Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/shell Nanocrystals Using Air Stable Reagents Via Successive Ion") require a high temperature (>250°C for selenides and >140°C for sulfides) to dissolve selenium in the reaction medium. Boron selenides readily dissolve in many solvents including amines, and hence the reaction temperature can be lowered significantly (~60°C) as found in the following experiment. The reaction temperature may be as low as room temperature and may even exceed the boiling point of the solvent. Preferably, the reaction mixture temperature is between about 40°C and about 130°C, more preferably between about 50°C and about 110°C, and more preferably between about 55°C and about 55°C and about 90°C. .

[0008] The much lower temperature should have great advantages over the previously known methods in that we can choose various solvents (even those with functional groups) and metal sources that are not stable or do not show desirable coordinating behavior at higher temperatures. The mixing of sulfur and selenium in the product particles is expected to be much easier than in the known methods. Thus the method is quite convenient. This method can be scaled up very easily.

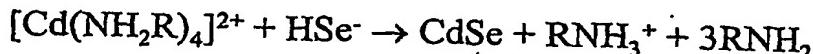
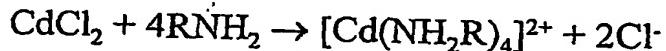
[0009] This new low-temperature preparation method for boron chalcogenides should work with various heating methods such as microwave heating. By controlling the power and duration period of microwave applied to the reaction container, we may be able to control the local reaction temperature (from about room temperature to the temperature above the boiling point of the solvent) and hence control the growth and crystallinity of the nanostructured materials. Other viable heating methods include but are not limited to ultrasonication (sonochemistry) and irradiation by other kinds of electromagnetic radiation (for example, infrared and UV-vis, s-ray and electron beam).

[0010] Uses of these nanoparticles include solar cell materials, nano-sensors, bio-probes, components in nano-electronic devices, optical materials and magneto-optical materials.

[0011] The new method has been proven to be successful in the preparation of photoluminescent CdSe nanoparticles as shown in the following example and figures.

#### Example

[0012] The reaction scheme is as follows:



E.g.:  $\text{RNH}_2 = \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{NH}_2$ : Oleyl amine

[0013] First, boron selenide ( $\text{B}_2\text{Se}_3$ ) was synthesized by heating a stoichiometric mixture of boron and selenium in a carbon-coated and evacuated silica tube. The product was transferred to a nitrogen-gas-filled glove box.  $\text{CdCl}_2$ , a cadmium source, was dissolved in an oleyl amine solution (technical grade) at 90°C. Separately, boron selenide was dissolved in an oleyl amine

solution at 90°C. These two solutions were cooled to room temperature, and the solutions remained clear, with no sign of precipitate. The two solutions were mixed at room temperature at a proper volume ratio to provide the correct stoichiometry for the target product, and the mixed solution remained clear. The solution mixture was taken from the glove box in a closed flask, was placed in a heating mantle and was heated gradually to 60°C, at which the solution changed its color suddenly, which indicated the initiation of nucleation. At 60°C, the growth of the particles are much slower (on the order of hours) and more controllable, which is advantageous over the earlier methods in which the particles fully form within several minutes. Thus, there is more controllable quenching of the growth and higher product yield. The reaction was quenched after desired periods of time (30 minutes, 5 hour, overnight and three days), and the flask was opened in air. An appropriate portion of ethanol was added to the product solution to flocculate and to precipitate the CdSe nanoparticles. After purification, the nanoparticles could be redispersed in cyclohexane. The x-ray powder diffraction patterns indicated pure zinc-blend type CdSe structure. The nanoparticles prepared at 200°C also are very small (6-10 nm). In addition, heating may be performed by microwave.

[0014] Additional experimental details and results are shown in the attached notebook pages.

What is claimed is:

1. A method of synthesizing metal chalcogenide particles, said method comprising the steps of:
  - a) providing a solution of a metal selenide;
  - b) providing CdCl<sub>2</sub> in an oleyl amine solution;
  - c) mixing the metal selenides solution with the CdCl<sub>2</sub> solution in the proper stoichiometric ratio to form a mixture solution at room temperature;
  - d) gradually heating the mixture solution to about 60°C and incubating the solution for a sufficient time for metal chalcogenide nanoparticles to form.

FIG. 1

## CdSe Nanoparticles (XRD Patterns)

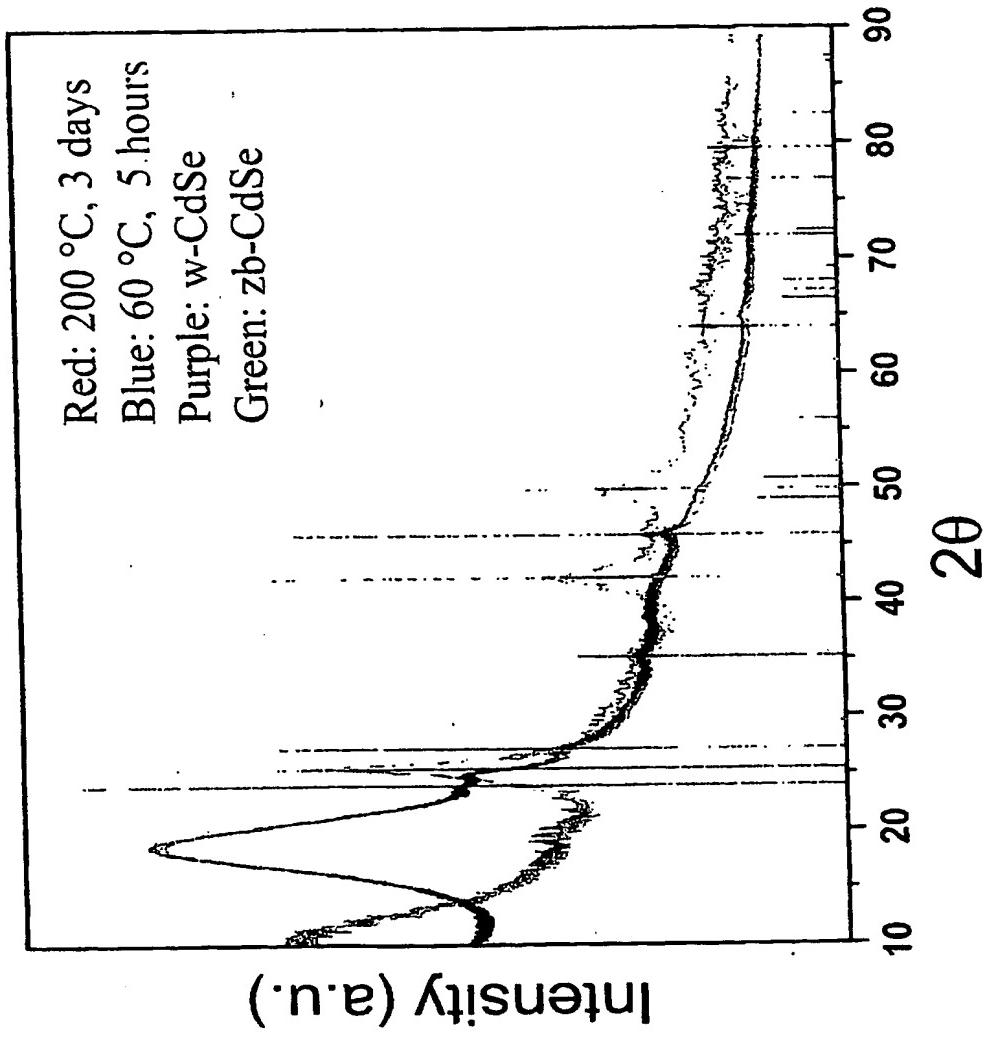


FIG. 2

CdSe Nanoparticles (60 °C, 5 Hours)

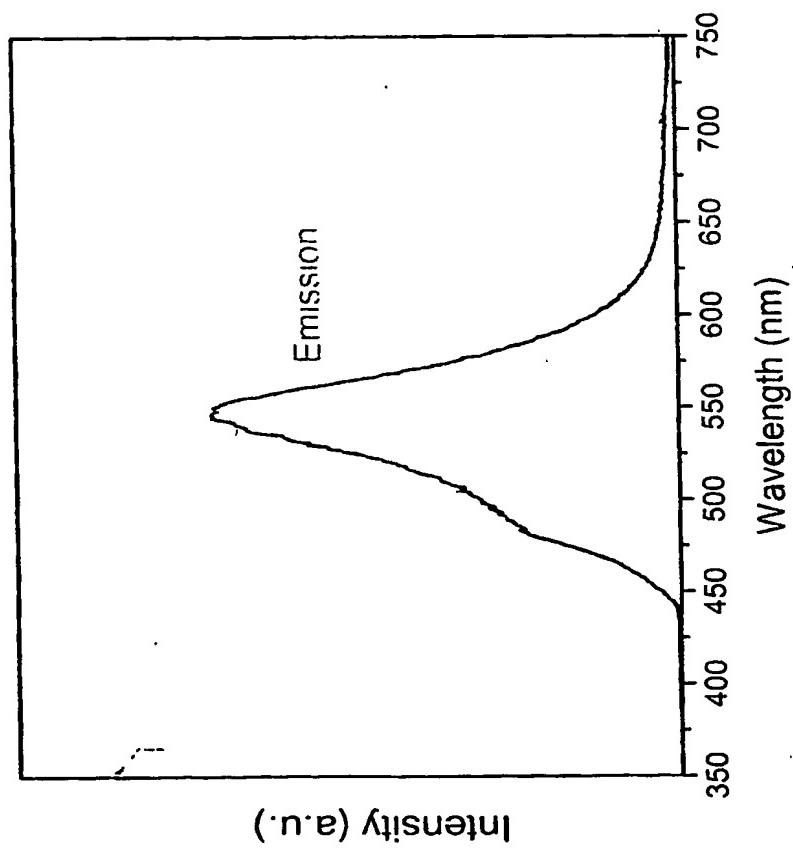


FIG. 3

CdSe Nanoparticles ( $60^{\circ}\text{C}$ , 3 Days)

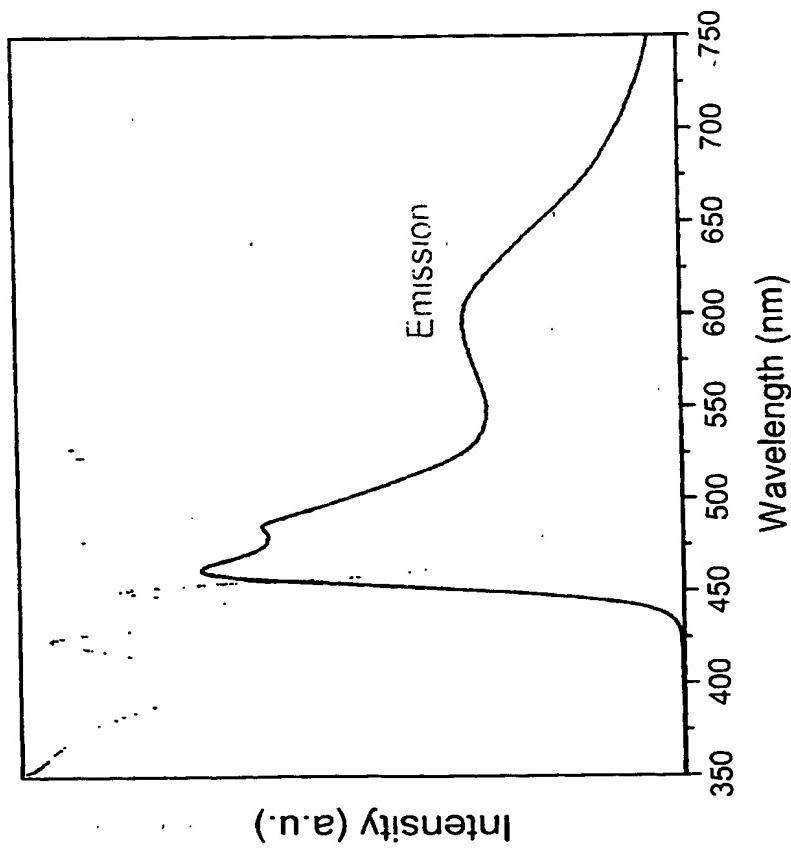


FIG. 4

CdSe Nanoparticles (200 °C, 3 Days)

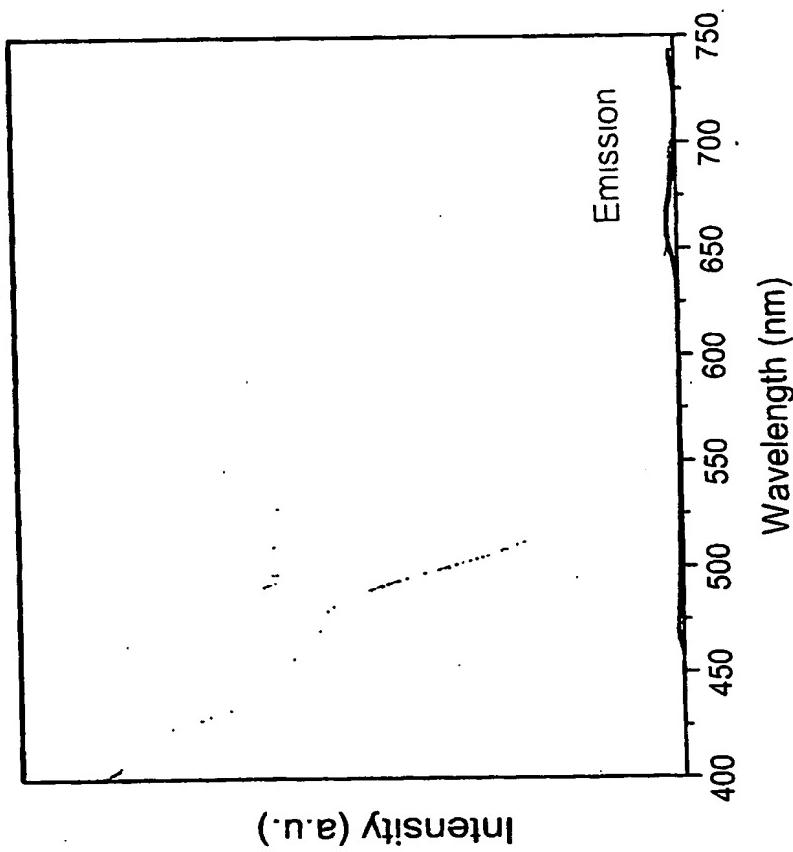
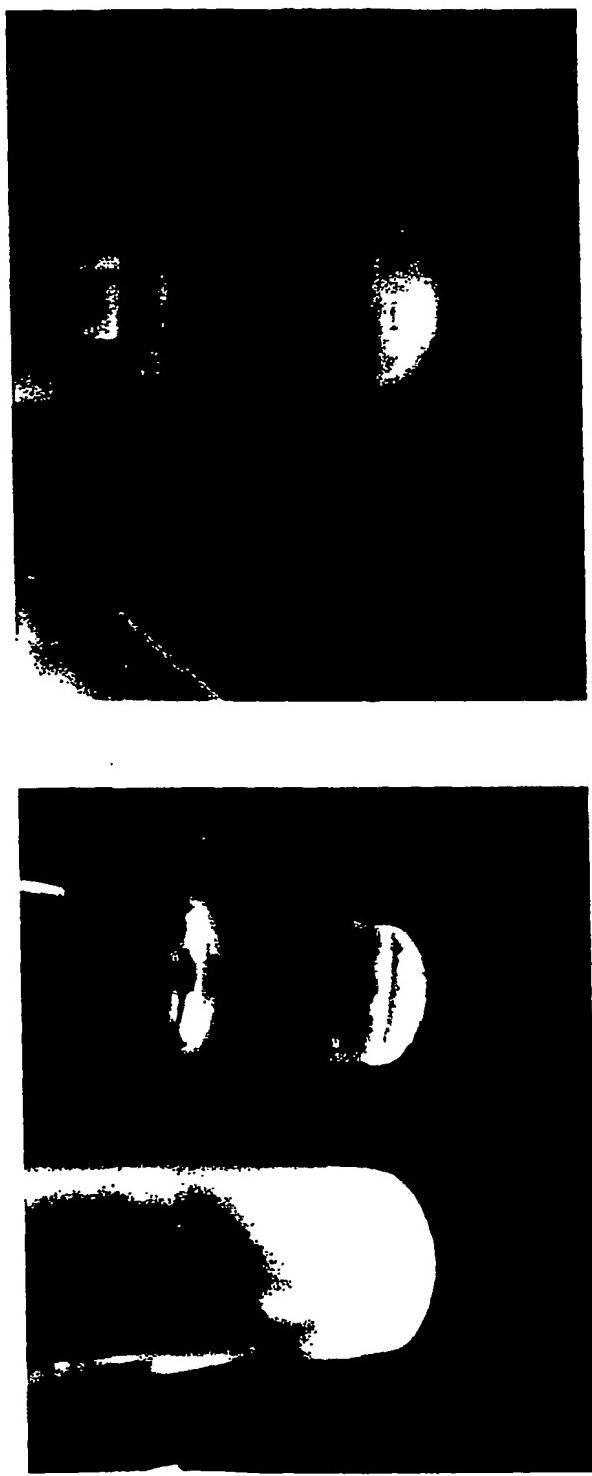


FIG. 5

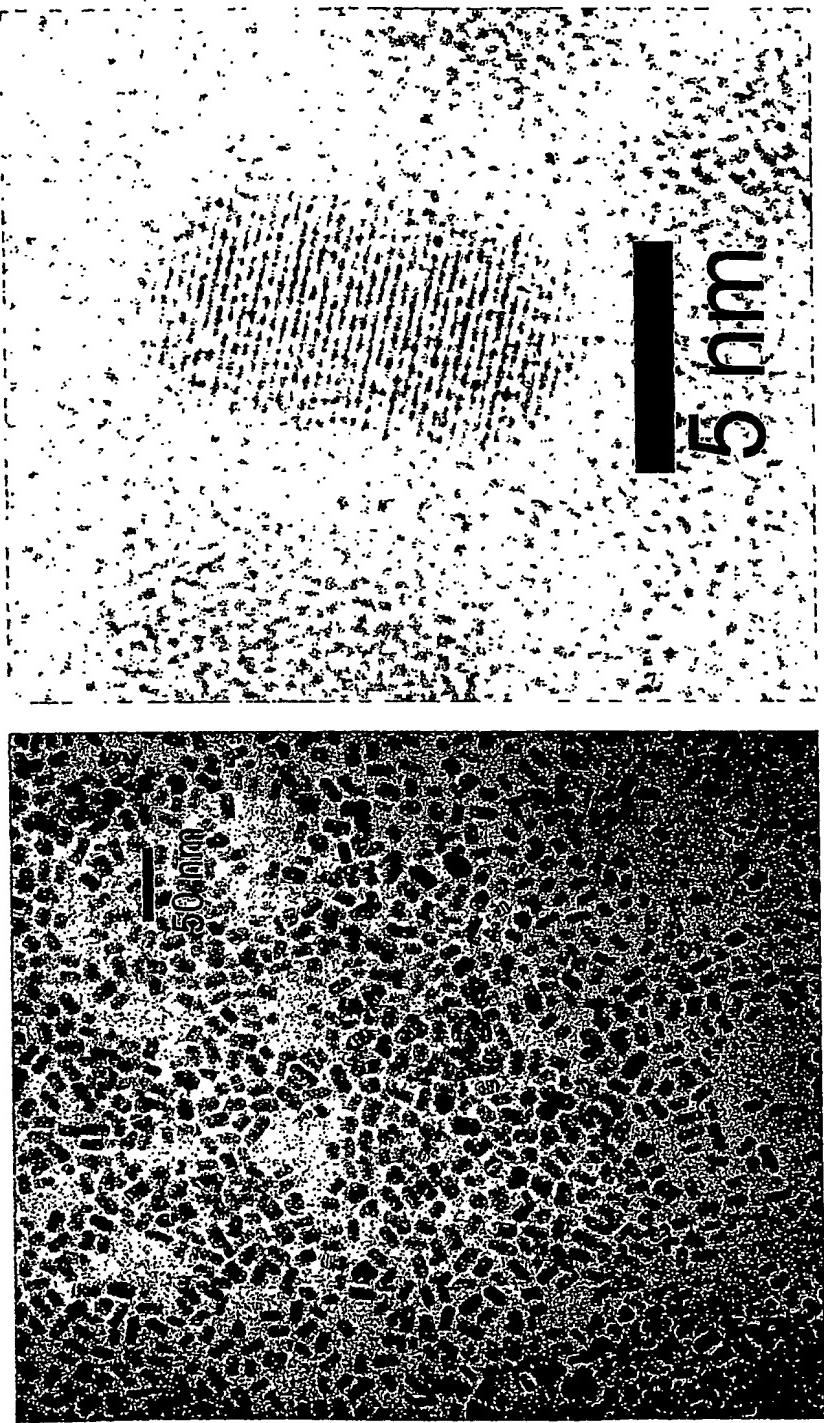
CdSe Nanoparticles ( $60^{\circ}\text{C}$ , 5 hours)



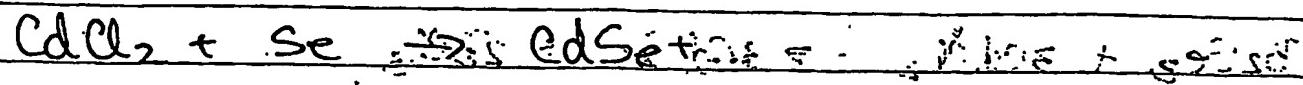
Excitation: 368 nm

FIG. 6

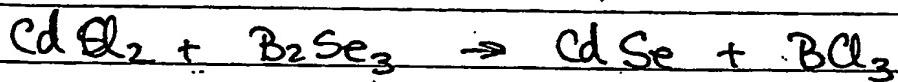
## CdSe Nanoparticles (200 °C, 3 Days)



DJECT R 134



[115. RAW]  $\Rightarrow$  CdSe · em

R 135

[116. RAW]  $\Rightarrow$  CdSe · em

R 136

CdCl<sub>2</sub> //  
(15 mL)

0.1 g B<sub>2</sub>Se<sub>3</sub> dissolved (over night) in 15 mL em.  
 $\Rightarrow$  dark sol. (black)

add ~~0.155~~<sup>0.213</sup> g CdCl<sub>2</sub>  $\Rightarrow$  yellow pp instantly

Solubility test:

6.66 g B<sub>2</sub>Se<sub>3</sub> in 1L em, @ RT.



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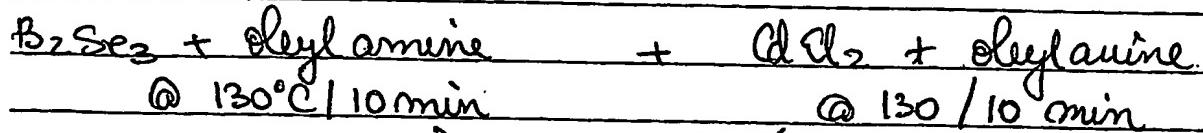
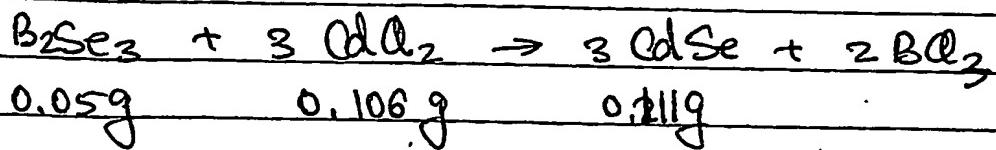
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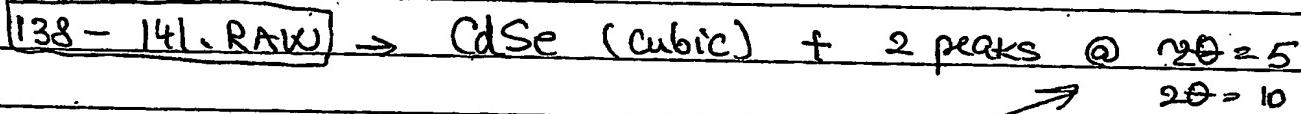
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dark-yellow  $\rightarrow$  orange sol.

100°C / 30 min.

dark orange sol.

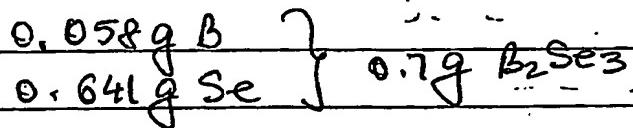
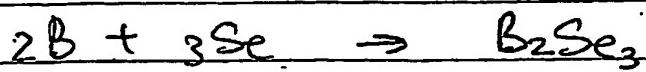


- sample washed w/  $\text{CH}_3\text{OH}$   $\checkmark$  XRD
  - redissolves in hexane

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## **R ad and Understood By**

R137 → R138



R139 CdSe

- $B_2Se_3$  in (cm) overnight → dark brown sol.
- +  $CdCl_2$ , ⇒ immediate yellow pp ⇒ overnight + shaking ⇒ yellow sol.
- opened in air ⇒ color of sol. changed to dark brown + yellow pp. on the bottom.
- washed pp. w/  $H_2O$ , alcohol,  $CS_2$ , alcohol. ⇒ yellow pp.

CdSe O2. RAW

CdSe · (cm) ?

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Date

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Date

R 140-a CdSe.

$\text{B}_2\text{Se}_3$  in oleylamine  $\rightarrow$  orange color; solubility @ RT  
not great. (I)

$\text{CdCl}_2$  in oleylamine  $\Rightarrow$  good solubility (II)

(I) + (II)  $\Rightarrow$  bright-yellow sol.

+ Ethanol  $\Rightarrow$  centrifuged  $\Rightarrow$  yellow pp.

[RAW] - low 2θ peaks

R 140-b CdSe.CdSe TEM

$\text{B}_2\text{Se}_3$  in 5 mL oleylamine

heat in oven

mmoles of  $\text{B}_2\text{Se}_3 \rightarrow 1.55$  g  $\text{B}_2\text{Se}_3$

#  $\text{B}_2\text{Se}_3 : \text{CdCl}_2 =$   
 $\approx 7:1$

[USED]: 0.387 g  $\text{B}_2\text{Se}_3$

$\text{CdCl}_2$  in oleylamine (10 mL)

heat in oven

mmol  $\text{CdCl}_2 \rightarrow 0.182$  g  $\text{CdCl}_2$

[USED]: 0.0455 g  $\text{CdCl}_2$

bp. oleylamine = 199°C.

[RAW] CdSe  $\rightarrow$  2 peaks @  $2\theta = 6^\circ, 2\theta = 9^\circ$  Continued on Page

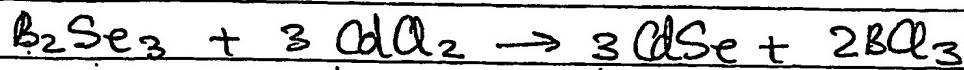
200°C

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- broad peaks
- good crystallinity
- TEM

JEC

R 141



0.19 g      0.213 g      0.222 g

- Guylamine.

→ CdSe (cubic) + "something else at low T.

→ washed w/  $\rightarrow \text{H}_2\text{O}$

$\rightarrow \text{R-OH}$

$\rightarrow \text{CS}_2$  reacts X } same powder

$\rightarrow \text{THF}$

$\rightarrow$  acetone

pattern.

122  $\rightarrow$  132. RAXI

150°C

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Signed

Date

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Date

90. T

R 145

CdSe

Notebook No. 09/19/03  
Continued From Page

3

6 OF 7

0.05 g  $\text{B}_2\text{Se}_3$   
in cyclohexylamine

+

0.106 g  $\text{CdCl}_2$ ,  
in cyclohexylamine

$50^{\circ}\text{C} / 24 \text{ h}$

brown sol.

- $60^{\circ}\text{C} / 3$  days
- UV-vis
- fluorescence
- small particles ( $\sim 6 \text{ nm}$ )
- washed w/  $\text{ROH}$  3 times  $\rightarrow$  centrifuged  $\rightarrow$
- $\rightarrow$  redispersed in cyclohexane.

09/19/03

initial solution: yellow  $\rightarrow$  brownish10:15 AM       $50^{\circ}\text{C}$       no color change11:00 AM       $60^{\circ}\text{C}$       darker sol. (same color)1:00 PM       $60^{\circ}\text{C}$       brown sol.2:20 PM       $85^{\circ}\text{C}$ 

09/20/03

7:30 AM       $60^{\circ}\text{C}$       dark brown + pp.

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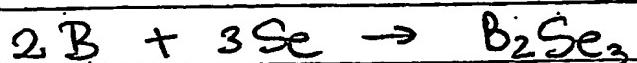
Date \_\_\_\_\_

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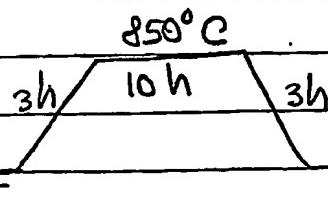
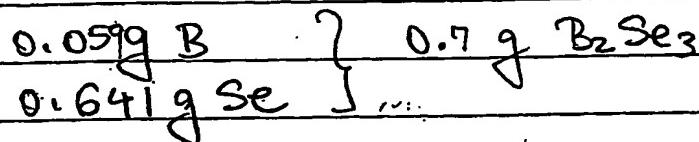
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PROJECT R 147, R 148

Note Book No. \_\_\_\_\_  
Continued From Page 10/04/03<sup>7</sup>



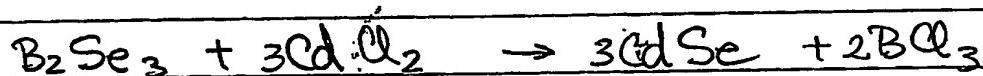
7 OF 7



- furnace #1

R 149 CdSe

10/06/03



$\text{B}_2\text{Se}_3$  (0.15g)  
in oleylamine  
(oven 12-3 h)

$\text{CdCl}_2$  (0.31g)  
+ in oleylamine  
(oven 12-3 h)

dark yellow - radish sol.

$60^\circ\text{C}$  / 3 h

color has change to orange

$60^\circ\text{C}$  / 3 h

same sol. color

- +  $\text{CH}_3\text{-OH}$  / centrifuged → retrieved particles → redispersed in cyclohexane (orange sol.)
- UV light → green → blue light

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